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Studies of structural and dielectric properties of $Ba_5BiTi_3Nb_7O_{30}$ ceramics

H SHARMA*, KIRAN KUMARI† and S N GIRI

Department of Physics, Veer Kunwar Singh University, Arrah 802 301, India
†Department of Physics, Dr S K S M College, Motihari 845 401, India

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Abstract. The polycrystalline samples of $Ba_5BiTi_3Nb_7O_{30}$ (hereafter BBTN) belonging to ferroelectric oxide family of tungsten bronze structure were prepared by high temperature solid-state reaction method. Preliminary X-ray analysis of the samples provided the lattice parameters $a = 11{\cdot}9331$ Å, $b = 14{\cdot}9684$ Å, and $c = 7{\cdot}0193$ Å, and also formation of a single-phase orthorhombic structure at room temperature (303 K). Detailed studies of dielectric constant (ε) and loss (tan δ) as a function of frequency (500 Hz to 10 KHz) at room temperature and also as a function of temperature (liquid nitrogen to 160°C) show the dielectric anomaly and structural phase transition at 16·8°C.

Keywords. Tungsten bronze structure; X-ray diffraction; dielectric constant; phase transition.

1. Introduction

Barium bismuth titanium niobate (BBTN) (Lines and Glass 1977) having composition $Ba_5BiTi_3Nb_7O_{30}$ is a member of ferroelectric oxide family of tungsten bronze (TB) structure. The TB structure consists of a complex array of distorted BO_6 octahedra sharing corners in such a way that different types of interstices (A_1, A_2, B_1, B_2 and C) are available for cation substitution (Jamieson *et al* 1965). The polar axis of most of the members of TB family is normally c-axis. A wide variety and range of compounds of tungsten bronze (TB) type have been studied. Some niobates with TB structure such as barium sodium niobate and potassium lanthanum niobates (Van Uitert *et al* 1967) owing to their wide industrial applications have been studied. Studies of structural and electrical properties of some ferroelectric oxides of TB structure (Choudhary and Choudhary 1990) have been published. The electrical conductivity measurement of some of these compounds (Mishra *et al* 1996) also confirms the occurrence of offset near their transition temperatures. An extensive literature survey reveals that even though the compound (BBTN) has been suggested to be a ferroelectric material (Lines and Glass 1977), no detailed study has yet been carried out either of its synthesis or of the establishment of its ferroelectric properties. We, therefore, present in this paper the synthesis, structural characterization and dielectric (dielectric constant (ε) and loss (tan δ)) properties of the titled compound.

*Author for correspondence

2. Experimental

The polycrystalline samples of BBTN were synthesized by the conventional high temperature solid-state reaction method from the following materials TiO_2 (99% S D fine chemical Pvt. Ltd), Nb_2O_5 (99% SMP), Bi_2O_3 (AG) and $BaCO_3$ (M/s Ultra Pure LOBA CHEMIE) in suitable proportion. These oxides and carbonates were thoroughly mixed in agate-mortar in air atmosphere for 5 h to get homogeneous mixture. The BBTN was obtained by repeated mixing and calcination at 1000°C for 30 h. The formation of the titled compound was checked by X-ray diffraction technique.

Cylindrical pellets (of diameter 11·2 mm and thickness 1–2 mm) were obtained under pressure of 5×10^7 kg/cm^2, using hydraulic press. These pellets were sintered in air atmosphere at 1100°C for 18 h. After polishing and grinding, both the flat surfaces of the pellets were electroded with air drying silver paints for electrical measurements. The density of pellets thus obtained was ~ 96% of its theoretical value.

The X-ray diffractogram (figure 1) of the BBTN pellet sample was taken with CuKα radiation ($\lambda = 1{\cdot}5418$ Å) in a wide 2θ range ($20° \leq 2\theta \leq 70°$) with Philips powder diffractometer (PW1710 Holland). The dielectric constant (ε) and loss (tan δ) of sintered and electroded pellet samples were obtained as function of frequencies (500 Hz–10 KHz) and temperatures (liquid nitrogen to 160°C), using GR 1620 capacitance measuring assembly.

3. Results and discussion

All the peak profiles of the BBTN samples were indexed with different cell configurations and a suitable cell with

its lattice parameters was then refined using least-squares technique. Using refined cell parameters, indexed reflections, and wavelength of CuKα radiation, interplanar spacing (d) of all the 24 reflections was calculated and compared with the respective observed values (table 1). A good match between calculated and observed d-values suggest that the compound is orthorhombic with lattice parameters $a = 11{\cdot}9331$ Å, $b = 14{\cdot}9684$ Å, and $c = 7{\cdot}0193$ Å at room temperature. It is however not possible to find out the space group with the limited data. The fair match also reflects the good quality of sample formation in terms of its chemical homogeneity. The linear particle size of the sintered sample calculated for strong, medium, and weak reflections scattered in a wide 2θ range using Scherrer's formula was nearly 20 nm which is in agreement with the value obtained from the particle size analyser.

Figure 2 shows the variation of dielectric constant (ε) and loss (tan δ) with frequencies at room temperature (303 K) indicating a normal behaviour of a dielectric

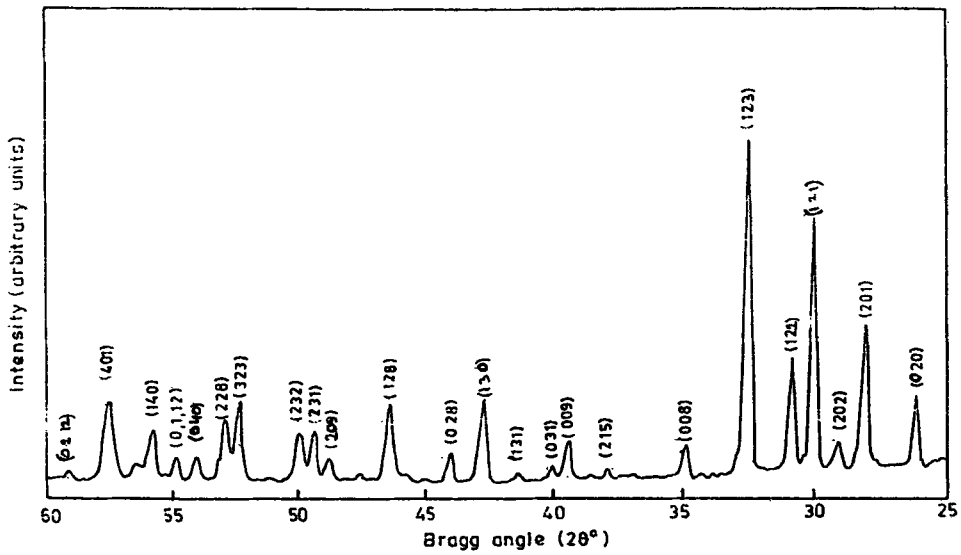

Figure 1. Room temperature X-ray diffraction pattern of $Ba_5BiTi_3Nb_7O_{30}$ (BBTN).

Table 1. Comparison of observed and calculated d-values (Å) of some reflections of BBTN at room temperature.

h	k	l	d_{obs}	d_{cal}	I/I_0
0	2	0	3·404	3·404	27
2	0	1	3·177	3·177	46
2	0	2	3·071	3·071	16
1	2	1	2·980	2·979	77
1	2	2	2·886	2·889	38
1	2	3	2·756	2·756	100
0	0	8	2·572	2·584	78
2	1	5	2·377	2·378	9
0	0	9	2·290	2·295	16
0	3	1	2·258	2·258	9
1	3	1	2·129	2·128	7
1	3	0	2·119	2·119	27
0	2	8	2·059	2·058	13
1	2	8	1·958	1·959	27
2	0	9	1·866	1·867	11
2	3	1	1·844	1·845	18
2	3	2	1·825	1·825	18
3	2	3	1·750	1·754	27
2	2	8	1·734	1·733	20
0	4	0	1·702	1·702	11
0	1	12	1·671	1·670	11
1	4	0	1·646	1·645	18
4	0	1	1·602	1·602	27
0	2	12	1·538	1·537	12

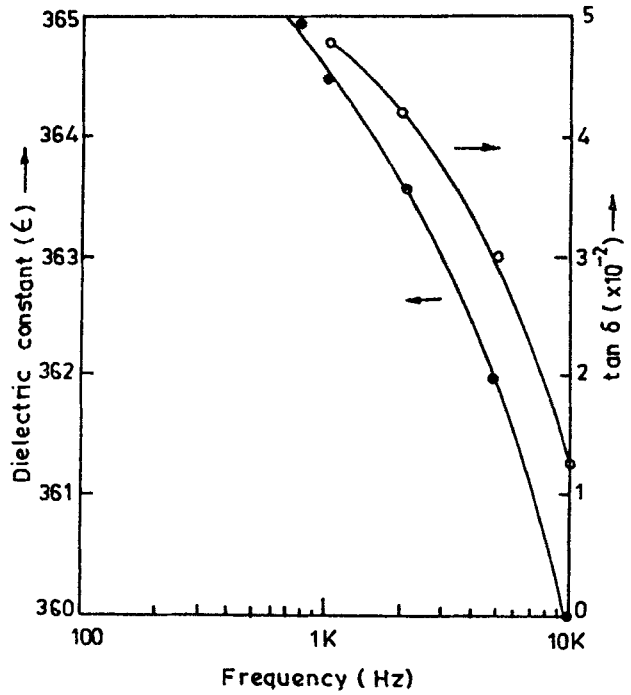

Figure 2. Variation of dielectric constant (ε) and loss (tan δ) of BBTN as a function of frequency (500 Hz to 10 KHz) at room temperature (303 K).

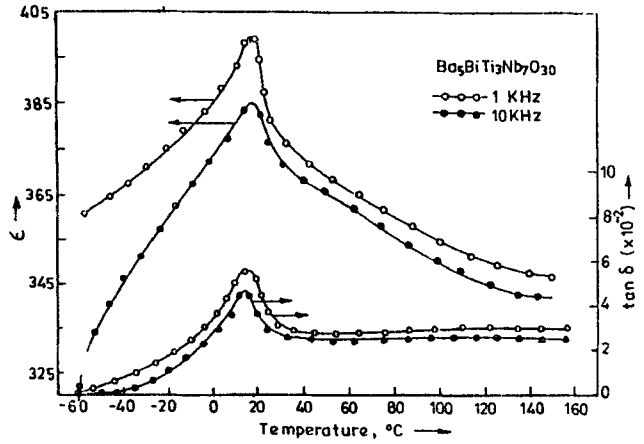

Figure 3. Variation of dielectric constant of BBTN as a function of temperature at two frequencies (1 KHz and 10 KHz).

(Bera and Choudhary 1995). We have also measured the variation of ε and tan δ with temperature at two different frequencies (1 KHz and 10 KHz) from liquid nitrogen temperature up to 160°C. It was observed that both ε and tan δ were nearly constant from liquid nitrogen temperature to – 60°C. The variation from – 60°C to 160°C is shown in figure 3. The presence of an anomaly around 16·8°C indicates the possibility of the compound being ferroelectric. Although the variation of dielectric constant with temperature appears to be diffuse, it is however not of the type usually reported for relaxor ferroelectrics (Cross 1987). In relaxor ferroelectrics, the temperature at which tan δ peaks is invariably much lower than the temperature corresponding to the peak in the dielectric constant. This suggests that the compound under investigation is a normal ferroelectric. Moreover, as for the normal ferroelectrics, in this compound too, the dielectric constant (ε) increases gradually with increase of temperature up to transition temperature, 16·8°C and then it decreases. On the other hand, the variation of dielectric loss (tan δ) with temperature was found very small (0–0·05) up to transition temperature and thereafter the dielectric loss decreased up to 30°C before becoming almost constant up to the working temperature, 160°C. This is not unusual, since this has been reported in ferroelectric oxides by Shapin *et al* (1965), Choudhary and Choudhary (1990), and Choudhary *et al* (1993).

Summarily speaking, it may be said that the compound BBTN has been synthesized, characterized and its ferroelectric characteristics have been established in the present investigation. The orthorhombic lattice structure with $a = 11{\cdot}9331$ Å, $b = 14{\cdot}9684$ Å, and $c = 7{\cdot}0193$ Å establishes the structural characteristics of this compound. Evaluation of dielectric behaviour including dielectric constant (ε), and loss (tan δ) behaviour over frequency range spanning 500 Hz and 10 KHz has given a clear indication of ferroelectric phase transition as evidenced by well-defined peaks in ε and tan δ curves (figure 3).

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